

30,000 and 5 mol of molecular weight 50,000, with these molecular weights being used to calculate a number average molecular weight of 37,000.

Page 5 of the Environmental Protection Agency's Premanufacture Notification (PMN) form requires the maximum weight % below "500 molecular weight" and "1000 molecular weight." All these examples are instances where the term "molecular weight" itself is used distinct from "weight average molecular weight." Thus, Applicants submit that the term "molecular weight" by itself is well known in the art and not indefinite.

The occurrence of "weight average" molecular weight on page 4 and "Mw" at page 11, lines 1, 14 and 27, page 13 lines 1 and 26, and page 14, line 13 is due to a translation error which arose when Japanese Patent Application No. P2000-025747 was translated. It is clear that an error was made when the disclosure is considered overall. For instance, Example 1 refers to the bulk polymer having a weight average molecular weight of 1,020,000 (see page 10, lines 26-27), so it does not make any sense for the example to subsequently refer to an Mw of 100,000 or less (see page 11, lines 1-2). Clearly, the disclosure of 100,000 or less refers to a range of molecular weights, such as a portion of Fig. 1-3 in Billmeyer starting from the left side of the x-axis (the molecular weight axis) and moving to a molecular weight of 100,000. The requirement in the claims of having 10% by weight or less of components having a molecular weight of 100,000 or less is similar to the EPA's PMN requirement of a weight % below 500 molecular weight and a weight % below 1000 molecular weight. Since the EPA, a U.S. government agency recognizes "molecular weight," it is not seen why the Examiner in the PTO, another U.S. government agency, does not recognize "molecular weight."

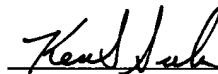
SUPPLEMENTAL RESPONSE UNDER 37 C.F.R. § 1.114  
U.S. Appln. No.: 09/918,532

In view of the above, it is submitted that the term "molecular weight" should be permitted by the Examiner and that the claims as amended in the Amendment filed July 18, 2003, should be entered and examined accordingly.

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,



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WASHINGTON OFFICE

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# TEXTBOOK OF POLYMER SCIENCE

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THIRD EDITION

**FRED W. BILLMEYER, JR.**

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Rensselaer Polytechnic Institute, Troy, New York*

A Wiley-Interscience Publication

**John Wiley & Sons**

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TABLE 1-4. Cohesive Energy Densities of Linear Polymers\*

Polymer	Repeat Unit	Cohesive Energy Density (J/cm <sup>3</sup> )
Polyethylene	—CH <sub>2</sub> CH <sub>2</sub> —	259
Polyisobutylene	—CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> —	272
Polyisoprene	—CH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> —	280
Polystyrene	—CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> )—	310
Poly(methyl methacrylate)	—CH <sub>2</sub> C(CH <sub>3</sub> )(COOCH <sub>3</sub> )—	347
Poly(vinyl acetate)	—CH <sub>2</sub> CH(OCOCH <sub>3</sub> )—	368
Poly(vinyl chloride)	—CH <sub>2</sub> CHCl—	381
Poly(ethylene terephthalate)	—CH <sub>2</sub> CH <sub>2</sub> OCOC <sub>6</sub> H <sub>4</sub> COO—	477
Poly(hexamethylene adipamide)	—NH(CH <sub>2</sub> ) <sub>6</sub> NHCO(CH <sub>2</sub> ) <sub>4</sub> CO—	774
Polyacrylonitrile	—CH <sub>2</sub> CHCN—	992

\*Walker (1952) and Small (1953).

properties typical of fibers, especially where molecular symmetry is favorable for crystallization. Chain stiffness or flexibility, referred to above, is largely determined by hindrance to free rotation about carbon-carbon single bonds in the polymer chain.

#### GENERAL REFERENCES

Ketelaar 1953; Cottrell 1958; Pauling 1960, 1964; Pimentel 1960; Chu 1967; Phillips 1970; Elias 1977, Part I.

#### D. MOLECULAR WEIGHT AND MOLECULAR-WEIGHT DISTRIBUTION

Perhaps the most important feature distinguishing polymers from low-molecular-weight species is the existence of a distribution of chain lengths and therefore degrees of polymerization and molecular weights in all known polymers (except possibly some biological macromolecules). This distribution can be illustrated by plotting the weight of polymer of a given molecular weight against the molecular weight, as in Fig. 1-3.

Because of the existence of the distribution in any finite sample of polymer, the experimental measurement of molecular weight can give only an average value. Several different averages are important. For example, some methods of molecular-weight measurement in effect count the number of molecules in a known mass of material. Through knowledge of Avogadro's number, this information leads to the

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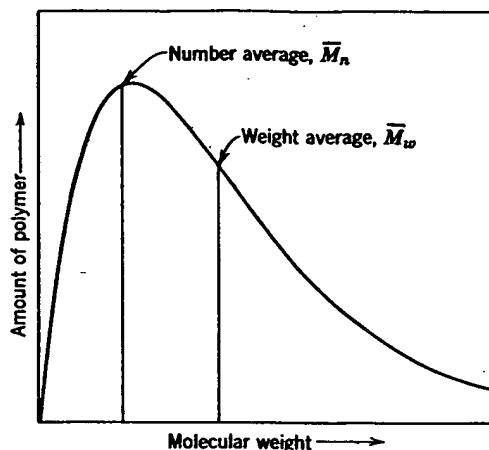


FIG. 1-3. Distribution of molecular weights in a typical polymer.

number-average molecular weight  $\bar{M}_n$  of the sample. For typical polymers the number average lies near the peak of the weight-distribution curve or the most probable molecular weight.

If the sample contains  $N_i$  molecules of the  $i$ th kind, for a total number of molecules  $\sum_{i=1}^{\infty} N_i$ , and each of the  $i$ th kind of molecule has a mass  $m_i$ , then the total mass of all the molecules is  $\sum_{i=1}^{\infty} N_i m_i$ . The number-average molecular mass is

$$\bar{m}_n = \frac{\sum_{i=1}^{\infty} m_i N_i}{\sum_{i=1}^{\infty} N_i} \quad (1-1)$$

and multiplication by Avogadro's number gives the number-average molecular weight (mole weight);

$$\bar{M}_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \quad (1-2)$$

Number-average molecular weights of commercial polymers usually lie in the range 10,000–100,000, although some materials have values of  $\bar{M}_n$  10-fold higher, and others 10-fold lower. In most cases, however, the physical properties associated with typical high polymers are not well developed if  $\bar{M}_n$  is below about 10,000.

After  $\bar{M}_n$ , the next higher average molecular weight that can be measured by absolute methods is the weight-average molecular weight  $\bar{M}_w$ . This quantity is defined as

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \quad (1-3)$$

TABLE 1-5. Typical Ranges of  $\bar{M}_w/\bar{M}_n$  in Synthetic Polymers\*

Polymer	Range
Hypothetical monodisperse polymer	1.000
Actual "monodisperse" "living" polymers	1.01-1.05
Addition polymer, termination by coupling	1.5
Addition polymer, termination by disproportionation, or condensation polymer	2.0
High conversion vinyl polymers	2-5
Polymers made with autoacceleration	5-10
Addition polymers prepared by coordination polymerization	8-30
Branched polymers	20-50

\*Billmeyer (1977).

It should be noted that each molecule contributes to  $\bar{M}_w$  in proportion to the square of its mass: A quantity proportional to the first power of  $M$  measures only concentration, and not molecular weight. In terms of concentrations  $c_i = N_i M_i$  and weight fractions  $w_i = c_i/c$ , where  $c = \sum_{i=1}^{\infty} c_i$ ,

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} c_i M_i}{c} = \sum_{i=1}^{\infty} w_i M_i \quad (1-4)$$

Unfortunately, there appears to be no simple analogy for  $\bar{M}_w$  akin to counting molecules to obtain  $\bar{M}_n$ .

Because heavier molecules contribute more to  $\bar{M}_w$  than light ones,  $\bar{M}_w$  is always greater than  $\bar{M}_n$ , except for a hypothetical monodisperse polymer. The value of  $\bar{M}_w$  is greatly influenced by the presence of high-molecular-weight species, just as  $\bar{M}_n$  is influenced by species at the low end of the molecular-weight distribution curve.

The quantity  $\bar{M}_w/\bar{M}_n$  is a useful measure of the breadth of the molecular-weight distribution curve and is the parameter most often quoted for describing this feature. The range of values of  $\bar{M}_w/\bar{M}_n$  in synthetic polymers is quite large, as illustrated in Table 1-5.

For some types of polymerization, the distribution of molecular weights (more often expressed as degrees of polymerization) can be calculated statistically; this topic is discussed in Chapter 3E. Experimental methods for measuring the molecular-weight averages defined above, among others, are the subject of Chapter 8.

#### GENERAL REFERENCES

Peebles 1971; Slade 1975; Billingham 1977.

#### BIBLIOGRAPHY

#### DISCUSSION

1. Define the of polym thermose
2. Discuss s how they lecular w
3. Consider  $M = 10^6$  adding th
  - a. 20 p
  - b. 20 p
 Calculate molecule
  - c. 20 p
  - d. 20 p
 Discuss molecule

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## DISCUSSION QUESTIONS AND PROBLEMS

1. Define the following terms: polymer, monomer, repeat unit, network, degree of polymerization, homochain polymer, heterochain polymer, thermoplastic, thermosetting, configuration, conformation.
2. Discuss some of the properties that make polymers useful materials, and show how they result from unique features of polymer structure such as high molecular weight. (This topic is amplified in later chapters.)
3. Consider three hypothetical monodisperse polymers, with  $M = 10,000$ ,  $M = 100,000$ , and  $M = 1,000,000$ . For each, calculate  $\bar{M}_w$  and  $\bar{M}_n$  after adding the following to 100 parts by weight  $c_i$  of the polymer with  $M = 100,000$ :
  - a. 20 parts by weight of the polymer with  $M = 10,000$ .
  - b. 20 parts by weight of the polymer with  $M = 1,000,000$ .

Calculate  $\bar{M}_w$  and  $\bar{M}_n$  after adding the following to 100 parts by number (of molecules) of the polymer with  $M = 100,000$ :

- c. 20 parts by number of the polymer with  $M = 10,000$ .
- d. 20 parts by number of the polymer with  $M = 1,000,000$ .

Discuss the dependence of  $\bar{M}_w$  and  $\bar{M}_n$  on the presence of high- and low-molecular-weight material.

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# POLYMER CHEMISTRY

## An Introduction

SECOND EDITION

Malcolm P. Stevens  
University of Hartford

OXFORD UNIVERSITY PRESS  
1990

New York Oxford  
OXFORD UNIVERSITY PRESS  
1990

## 2

# Molecular weight and polymer solutions

### 2.1 Number average and weight average molecular weight

Molecular weight is an extremely important variable because it relates directly to a polymer's physical properties. In general, the higher the molecular weight, the tougher the polymer; however (as will be shown in the next chapter), too high a molecular weight can lead to processing difficulties. What defines an optimum molecular weight depends in large measure on the chemical structure of the polymer and the application for which it is intended. In this chapter we will be concerned with molecular weight definitions, methods of determining molecular weight, and methods of determining the distribution of molecular weights in a polymer sample. We will reserve our discussion of molecular structure for the following chapter. We will also be concerned with solution properties of polymers, because solubility is prerequisite to molecular weight determination.

Given that polymers are high-molecular-weight compounds, we must begin with the question, what do we mean by high molecular weight? Where does low molecular weight end and high begin? There is no simple answer, because what constitutes a "low" molecular weight for a sample of polyethylene, for example, might be ideal for a sample of polyamide. Furthermore, some polymers are deliberately prepared with low molecular weight (even as oligomers) to facilitate initial processing, molecular weight being increased at a subsequent processing stage. In general, however, we think of polymers as having molecular weights that run from the low thousands up to the millions, with optimum molecular weight depending on chemical structure and application. Vinyl polymers of any commercial import normally have molecular weights in the range  $10^5$  to  $10^6$ . Polymers having very polar functional groups, such as polyamides, may have molecular weights as low as 15,000 to 20,000.

To determine molecular weights of simple (nonpolymeric) compounds, we employ the familiar techniques of mass spectrometry, freezing-point depression (cryoscopy), boiling-point elevation (ebulliometry), and, where suitable functional groups are present, titration (for example, neutralization or saponification equivalents). Determining molecular weights of polymers, how-

ever, is considered polymerization chains to terminate *average* molecular weights provided copy, ebulliometry molecular-weight polymers with many techniques of the polymer field because of the recent exciting developments in their traditional methods.

Techniques for polymers include although titration used in some cases determining molecular weight this is not an absolute the techniques can

Molecular weight of measurement properties (freezing-point depression) give rise because the number of molecules. The total weight molecular species

where  $N$  and  $M$  of each species sample per molecule

Suppose, for example, molecular weight

ever, is considerably more complex for two basic reasons. First, in any polymerization process, it is virtually impossible for all growing polymer chains to terminate at the same size; hence one must necessarily deal with average molecular weights. (Certain natural polymers having discrete molecular weights provide exceptions to this rule.) Second, the techniques of cryoscopy, ebulliometry, and titration are effective only with relatively low-molecular-weight polymers; more sophisticated methods must be used for polymers with molecular weights higher than about 40,000. The conventional techniques of mass spectrometry have not been used extensively in the polymer field beyond the characterization of polymer degradation products because of the requirements for volatilizable samples. Recent years have seen some exciting new developments in *field desorption* that have extended mass spectrometry into the macromolecular range. Such developments are, however, in their infancy and do not enjoy the routine applicability of the more traditional methods of molecular weight determination.

Techniques more commonly used for determining molecular weights of polymers include osmometry, light scattering, and ultracentrifugation, although titration (end-group analysis), cryoscopy, and ebulliometry are also used in some applications.<sup>1,2</sup> The most convenient method for routinely determining molecular weights involves measuring solution viscosities, but this is not an absolute method and can be used only in conjunction with one of the techniques of measuring absolute molecular weights.

Molecular weight values obtained depend in large measure on the method of measurement. Methods that depend on end-group analysis or colligative properties (freezing-point depression, boiling-point elevation, osmotic pressure) give rise to what is known as the number average molecular weight because the number of molecules of each weight in the sample are counted. The total weight of a polymer sample,  $w$ , is the sum of the weights of each molecular species present:

$$w = \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} N_i M_i$$

where  $N$  and  $M$  are the number of moles and molecular weight, respectively, of each species  $i$ . Number average molecular weight,  $\bar{M}_n$ , is the weight of sample per mole:

$$\bar{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i}$$

Suppose, for example, we have a polymer sample consisting of 9 mol of molecular weight 30,000 and 5 mol of molecular weight 50,000:

$$\bar{M}_n = \frac{(9 \times 30,000) + (5 \times 50,000)}{(9 + 5)} = 37,000$$

## 42 Polymer Structure and Properties

Suppose, instead, our sample consists of 9 g of molecular weight 30,000 and 5 g of molecular weight 50,000:

$$\bar{M}_n = \frac{(9 + 5)}{(9/30,000) + (5/50,000)} = 35,000$$

Light scattering and ultracentrifugation, on the other hand, are methods of determining molecular weight based on mass or polarizability of the species present. The greater the mass, the greater is the contribution to the measurement. In contrast to number average molecular weight (which is the summation of the *mole* fraction of each species times its molecular weight), these methods sum the *weight* fraction of each species times its molecular weight. The value thus obtained is called the *weight average molecular weight*,  $\bar{M}_w$ , and is expressed mathematically as

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

Consider the same two samples described previously. Nine mol of 30,000 molecular weight and 5 mol of 50,000 molecular weight:

$$\bar{M}_w = \frac{9(30,000)^2 + 5(50,000)^2}{9(30,000) + 5(50,000)} = 40,000$$

Substituting grams for moles:

$$\bar{M}_w = \frac{9(30,000) + 5(50,000)}{(9 + 5)} = 37,000$$

In each instance, we see that  $\bar{M}_w$  is greater than  $\bar{M}_n$ .

In measurements of colligative properties, each molecule contributes equally regardless of weight, whereas with light scattering, the larger molecules contribute more because they scatter light more effectively. It is for this reason that weight average molecular weights are always greater than number average molecular weights except, of course, when all molecules are of the same weight; then  $\bar{M}_w = \bar{M}_n$ . The narrower the molecular weight range, the closer are the values of  $\bar{M}_w$  and  $\bar{M}_n$ , and the ratio  $\bar{M}_w/\bar{M}_n$  may thus be used as an indication of the breadth of the molecular weight range in a polymer sample. This ratio is called the *polydispersity index*, and any system having a range of molecular weights is said to be *polydisperse*.

In our discussions of molecular weight measurement (Section 2.3), detailed descriptions of apparatus and derivations of working equations are not given. Students who wish to explore these areas in more detail are encouraged to consult the references provided. First, however, we will look briefly at *solution* properties of polymers because the various methods of determining molecular weight or molecular weight distribution depend on solubility and polymer-solvent interactions.

## 2.2 Polym

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The symbol  $\delta$  dissolve (nega be small. In Where  $\delta_1 = \delta_2$  solubility are solubility para densities.

# Part I -- GENERAL INFORMATION -- Continued

## Section B -- CHEMICAL IDENTITY INFORMATION -- Continued

### 2. Polymers (For a definition of polymer, see the Instructions Manual.)

Confidential

- a. Indicate the number-average weight of the lowest molecular weight composition of the polymer you intend to manufacture. Indicate maximum weight percent of low molecular weight species (not including residual monomers, reactants, or solvents) below 500 and below 1,000 absolute molecular weight of that composition.

Describe the methods of measurement or the basis for your estimates: GPC ☐ Other ☐ : (Specify) \_\_\_\_\_

i) lowest number average molecular weight: \_\_\_\_\_

ii) maximum weight % below 500 molecular weight: \_\_\_\_\_

iii) maximum weight % below 1000 molecular weight: \_\_\_\_\_

☐ Mark (X) this box if you attach a continuation sheet.

- b. You must make separate confidentiality claims for monomer or other reactant identity, composition information, and residual information. Mark (X) the "Confidential" box next to any item you claim as confidential.

- (1) -- Provide the specific chemical name and CAS Registry Number (if a number exists) of each monomer or other reactant used in the manufacture of the polymer.
- (2) -- Mark (X) this column if entry in column (1) is confidential.
- (3) -- Indicate the typical weight percent of each monomer or other reactant in the polymer.
- (4) -- Mark (X) the identity column if you want a monomer or other reactant used at two weight percent or less to be listed as part of the polymer description on the TSCA Chemical Substance Inventory.
- (5) -- Mark (X) this column if entries in columns (3) and (4) are confidential.
- (6) -- Indicate the maximum weight percent of each monomer or other reactant that may be present as a residual in the polymer as manufactured for commercial purposes.
- (7) -- Mark (X) this column if entry in column (6) is confidential.

Monomer or other reactant and CAS Registry Number (1)	Confidential (2)	Typical composition (3)	Identity Mark (X) (4)	Confidential (5)	Maximum residual (6)	Confidential (7)
		%			%	
		%			%	
		%			%	
		%			%	
		%			%	
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		%			%	

☐ Mark (X) this box if you attach a continuation sheet.

- c. Please identify which method you used to develop or obtain the specified chemical identity information reported in this notice. (check one).
- ☐ Method 1 (CAS Inventory Expert Service - a copy of the identification report obtained from CAS Inventory Expert Service must be submitted as an attachment to this notice) ☐ Method 2 (other source)

- d. The currently correct Chemical Abstracts (CA) name for the polymer that is consistent with TSCA Inventory listings for similar polymers.

- e. Provide a correct representative or partial chemical structure diagram, as complete as can be known, if one can be reasonably ascertained.

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